

Title: A General Techno-Economic Analysis of CO₂ Electrolysis Systems

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Abstract

The electrochemical reduction of carbon dioxide (CO₂) has received significant attention in academic research, although the techno-economic prospects of the technology for the large-scale production of chemicals are unclear. In this work, we briefly reviewed the current state-of-the-art CO₂ reduction figures of merit, and performed an economic analysis of a generalized CO₂ electrolyzer system for the production of 100 tons/day of various CO₂ reduction products. While carbon monoxide and formic acid were the most economically favorable products under current conditions, higher-order alcohols such as ethanol and n-propanol could be highly promising if reasonable electrocatalytic performance benchmarks were achieved. Herein, we established performance targets such that if these targets are achieved, electrochemical CO₂ reduction for fuels and chemicals production can become a profitable option as part of the growing renewable energy infrastructure.

1. Introduction

Atmospheric carbon dioxide (CO₂) emissions have recently reached the highest levels in human history. It is widely believed that failure to curb these rising emissions could lead to potentially devastating climate change effects.¹ Mitigating CO₂ emissions on a global scale remains a major challenge since the global population, and subsequently the global energy usage, is projected to continue to increase. Although renewable energy sources such as wind and solar are beginning to gain more market share, fossil fuel resources will continue to be the dominate energy source through the mid-century. A major driver for this is the continued dependence of the transportation and chemical sectors on fossil fuels. For example, the U.S. Energy Information Administration (EIA) estimated that while renewable sources will account for over 27% of electricity generation by 2040, renewable energy in the transportation and chemical sectors will only be <1% and 9%, respectively.² This is because petroleum-based vehicles will continue to dominate economically, and fossil fuel sources will continue to be a critical chemical feedstock in the near future.

The conversion of CO₂ into fuels and chemicals using renewable electricity is one promising method of increasing the penetration of renewables into the fuels and chemicals industry.³⁻⁵ CO₂ conversion can be performed through biological, thermochemical, photochemical, and electrochemical means, each of which has been widely studied.⁶⁻⁸ Electrochemical conversion of CO₂ has several advantages including: fine control of reaction rates/selectivities through the applied voltage, wide scalability due to modular electrolyzer designs, and excellent coupling to intermittent renewable energy sources. With this process, carbon-neutral electricity sources such as wind, solar, and nuclear can be used to electrochemically reduce CO₂ to valuable fuels and chemicals, thus closing the carbon loop and reducing CO₂ emissions.

In recent years, there has been a remarkable increase in studying electrochemical CO₂ reduction (eCO₂R). Most research has been focused on the fundamental understanding of the catalysis and reaction mechanisms, while other works involved the design of lab-scale CO₂ electrolyzer flow systems.⁹⁻¹³ However, there has been limited efforts related to understanding the feasibility of this technology as a means of producing fuels and chemicals on a techno-economic basis, as well as what role eCO₂R could play in the future renewable energy infrastructure. Some researchers have raised questions regarding the potential of CO₂ reduction to mitigate CO₂ emissions at an appreciable level, and whether the process can be performed in an economical way competitive to traditional chemical manufacturing processes.¹⁴ In this work, we reviewed the historical performance trends for the electrochemical reduction of CO₂ to commonly reported CO₂ reduction products. Next, we developed a techno-economic model for a generalized eCO₂R plant. Using this model, we analyzed the economic viability of various reduction products under current and future conditions and proposed performance targets to enable the profitable production of these products. Finally, we considered the role eCO₂R can play in reducing greenhouse gas emissions as part of the future renewable energy infrastructure.

2. CO₂ Reduction Products

The electrochemical reduction of CO₂ can proceed through a two-, four-, six-, eight-, twelve-, or even an eighteen-electron reduction pathway to produce various gaseous products (carbon monoxide, methane, and ethylene) and liquid products (formic acid, methanol, ethanol, and propanol). Table 1 summarizes seven common CO₂ electrochemical reduction products and

their half-cell electrochemical reactions as well as the thermodynamic electrode potentials versus the standard hydrogen electrode (V vs SHE) under standard conditions, calculated from the standard Gibbs free energies. Others have also reported up to sixteen different CO₂ reduction products including glyoxal, ethylene glycol, acetaldehyde, propionaldehyde, etc.¹⁵⁻¹⁶ However, these products are either reported as trace amounts or uncommon; and thus, the seven major products listed in Table 1 are the main focus. In addition, if CO₂ reduction is performed in aqueous environment, then the undesirable hydrogen evolution reaction also occurs in competition to the CO₂ reduction reaction (also listed in Table 1).

Table 1: Selected standard potentials for the electrochemical reduction of CO₂

Half-Cell Electrochemical Reactions	Potential (V vs SHE)
$\text{CO}_{2(g)} + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{CO}_{(g)} + \text{H}_2\text{O}_{(l)}$	-0.106
$\text{CO}_{2(g)} + 2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{HCOOH}_{(l)}$	-0.250
$\text{CO}_{2(g)} + 6\text{H}^+ + 6\text{e}^- \leftrightarrow \text{CH}_3\text{OH}_{(l)} + \text{H}_2\text{O}_{(l)}$	0.016
$\text{CO}_{2(g)} + 8\text{H}^+ + 8\text{e}^- \leftrightarrow \text{CH}_4_{(g)} + 2\text{H}_2\text{O}_{(l)}$	0.169
$2\text{CO}_{2(g)} + 12\text{H}^+ + 12\text{e}^- \leftrightarrow \text{C}_2\text{H}_4_{(g)} + 4\text{H}_2\text{O}_{(l)}$	0.064
$2\text{CO}_{2(g)} + 12\text{H}^+ + 12\text{e}^- \leftrightarrow \text{C}_2\text{H}_5\text{OH}_{(l)} + 3\text{H}_2\text{O}_{(l)}$	0.084
$3\text{CO}_{2(g)} + 18\text{H}^+ + 18\text{e}^- \leftrightarrow \text{C}_3\text{H}_7\text{OH}_{(l)} + 5\text{H}_2\text{O}_{(l)}$	0.095
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_{2(g)}$	0.000

As shown in Table 1, CO₂ can be electrochemically reduced to several products at similar potentials, and thus, a critical equation arises: which CO₂ reduction product should be targeted for commercialization? The answer to this question greatly depends on economics, the supply and demand of certain products, which indirectly relates to the current state-of-the-art technologies that can affect the overall costs and production rates. To help facilitate this discussion, the market price (US \$ kg⁻¹) of the seven CO₂ reduction products are listed in Table 2 and these values were taken and averaged from various sources including the Independent Chemical Information Service (ICIS), U.S. EIA and various published works.¹⁷⁻¹⁹ The market price was also normalized to the number of required electrons to incorporate the electrical cost to produce each product since ideally, electrical energy will be used to drive the reduction of CO₂. Lastly, the annual global production of each product was also tabulate, which reflect the market capacity and demand for each product and were also taken from various sources including the U.S. Department of Energy (DOE), private company/organization websites, and various published works.²⁰⁻²⁴

In the case of carbon monoxide (CO), it was broken down into two sub-products, syngas and pure CO, since majority of industrially produced CO is in the form of syngas and is typically produced in-line with downstream gas-to-liquid processing units. Interestingly, although formic acid had the highest normalized market price (16.1 x 10⁻³ \$ electron⁻¹), which is reflected by the number of electrons needed to produce formic acid, the annual production of formic acid was the second to

lowest (0.6 million metric tons per year). This value reflects the limited industrial use of formic acid as preservative and antibacterial agent. On the contrary, being a major source for power generation and domestic heating as well as having abundant sources of natural gas, methane had the highest annual production (250 million metric tons per year) and the lowest normalized market price (0.4×10^{-3} \$ electron⁻¹). Turning to n-propanol, although this chemical is an industrially important chemical precursor, it had the lowest annual production (0.2 million metric tons per year) because it is limited by the difficulty in production. However, if n-propanol could be efficiently produced through CO₂ reduction, it could supplant ethanol as a transportation fuel additive due to its higher energy density, greatly increasing its potential market share. From Table 2, it can be concluded that the highly desirable products include ethylene, methanol, ethanol, and syngas since these products have high market capacity as well as decent normalized market prices. These four products have major industrial uses as chemical precursors, fuel additives, and fuel for energy generation. It must be noted that these values were organized from an economic perspective to facilitate the following discussion about the economic analysis of the CO₂ electrochemical reduction process. The overall assessment of which product is the most desirable for CO₂ electrolysis technology will take the state-of-the-art technologies such as catalyst, electrochemical reactor design, separation, and storage into account.

Table 2: Market price and annual global production of major CO₂ reduction products

Product	Number of Electrons	Market Price (\$/kg)	Normalized Price (\$/electron) X 10 ³	Annual Global Production (Mtonne)
Carbon monoxide (syngas)	2	0.06	0.8	150.0
Carbon monoxide	2	0.6	8.0	-
Formic acid	2	0.70	16.1	0.6
Methanol	6	0.60	3.1	110.0
Methane	8	0.18	0.4	250.0
Ethylene	12	1.30	3.0	140.0
Ethanol	12	1.00	3.8	77.0
n-Propanol	18	1.40	4.8	0.2

3. Figures of Merit

The CO₂ molecule is a fully oxidized and thermodynamically stable and thus catalysts are needed to help facilitate the chemical transformation to minimize the energy penalty required to reduce CO₂. The study of catalysts for the electrochemical reduction of CO₂ can be dated back to the mid-1980s when Hori *et al.* completed a comprehensive study on various transition-based metal electrodes to determine their selectivity as well as their catalytic activity towards different CO₂ reduction products.²⁵⁻²⁶ Metals such as Au, Ag, and Zn were discovered to be selective towards producing CO while metals such as Pb and Sn were selective towards producing formic

acid. Interestingly, Cu was the only metal that could reduce CO₂ to C₂ hydrocarbons and alcohols at appreciable levels. Since then, there have been significant efforts in developing new catalysts to improve selectivity, catalytic activity, and overall stability. These efforts include developing nanostructured catalysts to increase the number of active sites,²⁷⁻³¹ tuning selectivity by developing bimetallic catalysts,³²⁻³³ and even exploring catalysts beyond just simple metallics such as transition metal chalcogenides³⁴⁻³⁵ and even nitrogen-doped carbon-based materials that have shown interesting catalytic abilities.³⁶⁻³⁷ In addition, the choice of electrolyte, electrochemical reactor design, electrode preparation, and delivery of reactant and products to and from the active sites have also been studied to improve the overall performance of eCO₂R.^{10-11, 38-41}

In general, an efficient CO₂ electrolyzer requires not only highly active, stable, and selective catalysts, but also durable devices with minimal ohmic resistance and high mass transport properties under reacting conditions. The characterization of each individual feature of an electrolyzer is quite complex. However, there are several figures of merit that are commonly used to characterize the performance of an electrochemical system, namely current density, Faradaic efficiency, energetic efficiency, and stability.^{5, 42}

The current density is defined as the current flow divided by the active electrode area at a given potential. The most commonly used is the geometric area. The current density is a measure of the electrochemical reaction rate (catalytic activity) per area of electrode and is used to determine the overall electrode size needed to obtain a desired reaction rate. Furthermore, the current density is also dependent on multiple factors such as catalyst loading, utilization of the catalyst, and transport rate of reactants and products to and from the electrode. High current density is ideal since it minimizes the overall electrolyzer size and reduces capital investment for a desired production rate.

The Faradaic efficiency, also known as the current efficiency, for a given product is defined by the following equation:

$$\varepsilon_{Faradaic} = \frac{z \cdot n \cdot F}{Q} \quad (1)$$

where z is the number of required electrons to produce a given product, n is the number of moles of the given product, F is Faraday's constant, and Q is the total charged passed. In other words, the Faradaic efficiency of a given product is the selectivity of reducing CO₂ to that product. A high Faradaic efficiency is desired to minimize necessary separation processes that could dramatically increase the overall capital and operational costs.

The energetic efficiency is defined by the following question:

$$\varepsilon_{energetic} = \sum_i \frac{E_i^o \varepsilon_{i,Faradaic}}{E_i^o + n} \quad (2)$$

where E_i^o is the equilibrium cell potential for product i , $\varepsilon_{i,Faradaic}$ is the Faradaic efficiency of product i , and n is the total cell overpotentials including the anodic and cathodic kinetic activations, limited mass transports, and ohmic resistances. The energetic efficiency describes the ratio

between energy stored in the desired products versus input energy needed to produce those products. Qualitatively, a high energetic efficiency signifies a small energy penalty needed to produce the desired product.

The stability describes the gradual degradation/deactivation of the electrode catalyst and the overall electrochemical cell. Unfortunately, the durability of the electrochemical cell is probably the least studied aspect of electrochemical reduction of CO₂ and is strongly affected by the nature of working load and operating conditions. It has also been known that slight impurities in the electrolyte can significantly deactivate or alter the catalytic performance of CO₂ reduction catalysts. In regards to other related technologies, PEM water-splitting electrolyzers have shown to operate beyond 20,000 hrs under mild conditions; and therefore, CO₂ electrolyzers will probably need to operate with lifetimes of similar ranges.⁵ Overall, better stability will reduce maintenance and replacement costs as well as downtime during operation.

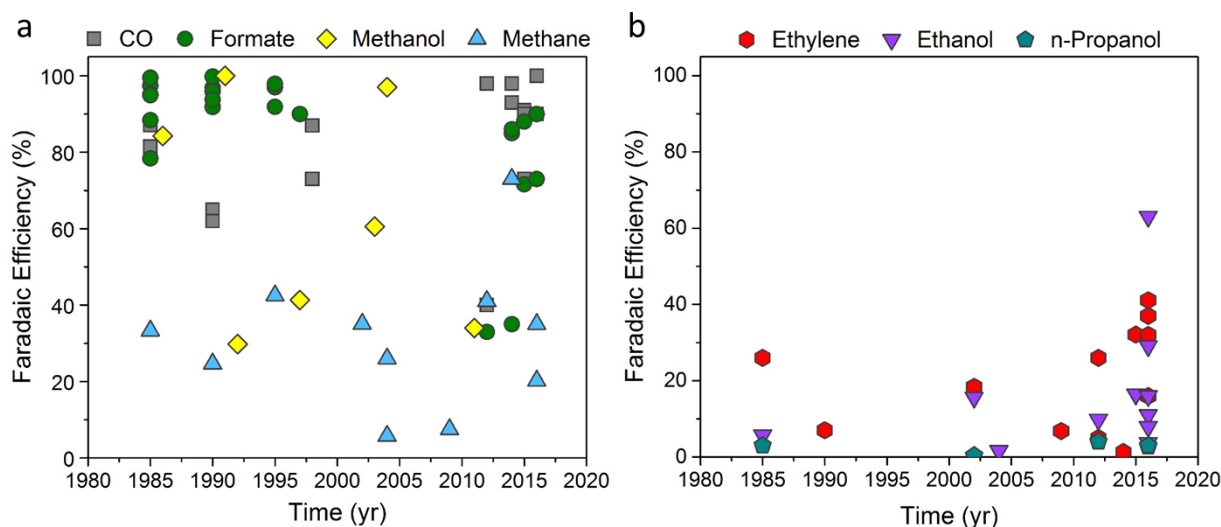


Figure 1: CO₂ reduction Faradaic efficiencies versus year (when reported) for a) C₁ and b) C₂-C₃ products.^{15, 25-28, 30-31, 33-37, 39, 43-72}

Figures 1 shows the general trends of Faradaic efficiencies towards various CO₂ reduction products versus time dating back to the comprehensive study published by Hori *et al.* in 1985 (C₁ products for Figure 1a and C₂-C₃ products for Figure 1b).²⁵⁻²⁶ Although both homogeneous and heterogeneous catalysts for CO₂ reduction have been reported, heterogeneous catalysts are the main focus of this review considering the robustness of the catalysts. It must be noted, that Figure 1 does not fully reflect the true performance of the state-of-the-art catalysts since some catalysts were able to achieve high selectivity (i.e., Faradaic efficiency) by sacrificing catalytic activity (i.e., current density) and vice-versa, which will be discussed in detail in the following section. In the case of C₁ products, Faradaic efficiencies for CO and formic acid have been consistently high (>80%) with majority of these catalysts being Ag and Sn-based for CO and formic acid production, respectively. In the case of methanol, only a few catalysts were reported to be methanol selective and the reported methanol Faradaic efficiencies varied greatly from 30% to 98%. On the contrary, methane Faradaic efficiencies have been consistently low (<50%) with majority of these catalysts being Cu-based. In the case of C₂ products, Faradaic efficiencies of ethylene and ethanol have, but

not until recently, been consistently low and majority of these catalysts were also Cu-based. However, in 2016, significant strides have been made on improving the Faradaic efficiency for C_2 products, achieving as high as 41% and 63% for ethylene and ethanol, respectively.⁶⁷ For the case of C_3 products, the Faradaic efficiency for n-propanol was still significantly low (<5%) which reflects the energy intensive (18 electrons) process and complex reaction pathway that requires multiple of carbon-carbon coupling.

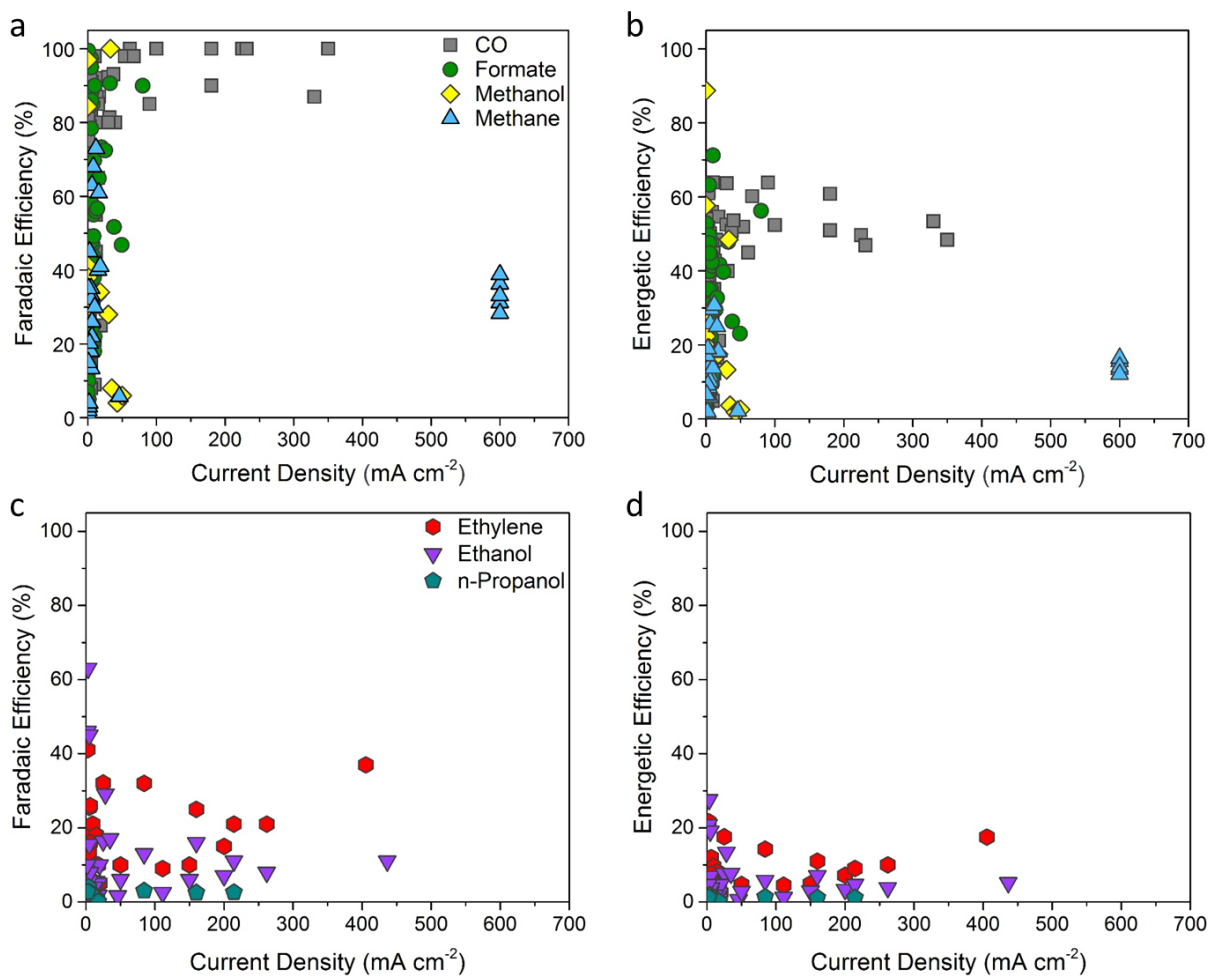


Figure 2: Faradaic efficiency versus current density for a) C_1 and c) C_2 - C_3 products and energetic efficiency versus current density for c) C_1 and d) C_2 - C_3 products.^{15, 25-28, 30-31, 33-37, 39, 43-72}

Figures 2a and c show the Faradaic efficiencies versus current density while Figures 3b and d show the energetic efficiencies for C_1 and C_2 - C_3 products versus current density, respectively. In the case of energetic efficiencies, majority of CO_2 reduction research only focused on the cathodic reaction and only reported the overpotential of the CO_2 reduction reaction. Because of this, the assessment assumed that the anodic reaction was the water oxidation reaction with a standard potential of 1.23 V vs SHE with an anode overpotential of 0.3 V, typical activation overpotential for the state-of-the-art oxygen evolution reaction catalyst.⁷³ It must be noted that each data point was not consistent with each other and varied in terms of type of catalyst, electrode preparation, electrochemical cell configuration, and operating conditions. With that in

consideration, Figure 2 aims to convey the general catalytic performance trends of various catalysts towards producing CO, formic acid, methanol, methane, ethylene, ethanol, and n-propanol. Overall, it has been difficult to simultaneously achieve high current density, Faradaic efficiency, and energetic efficiency, which illustrates that further efforts are needed to develop better CO₂ reduction catalysts. In general, high Faradaic efficiencies can be achieved at the expense of current densities, and majority of the energetic efficiencies for reduction CO₂ were less than 60%. It must be noted that majority of reported CO₂ reduction studies were conducted under short timescales (<5 hrs), and thus long term stability in the range of hundreds or even thousands of hours are unknown.

4. Model for CO₂ Electrolyzer System

Despite the significant amount of research that has been performed on eCO₂R catalysts and electrolyzers, there have been few technical and economic analyses that evaluate the potential and feasibility of implementing the CO₂ electrolyzer technology on a large scale. Previously, Perez-Forbes et al. analyzed the economic and environmental potential of CO₂ reduction to formic acid using ChemCAD simulations.⁷⁴ Li et al. investigated the greenhouse gas emission reductions and economic viability of an electrochemical CO₂ to CO system coupled with a Fischer-Tropsch process to produce synthetic fuels.⁷⁵ Furthermore, Verma et al. developed a gross-margin model to determine and compare the maximum feasible operating voltage for the production of various CO₂ electrolysis products.⁷⁶

Although these various investigations provide useful insights to the economic potential of CO₂ reduction, there still lacks a capital investment analysis of a general CO₂ electrolysis system, from which the return on capital investment and time-valued net present value for the production of the most commonly reported products can be determined. Due to the lack of commercially developed analogues for a CO₂ reduction process, a highly detailed analysis is difficult. However, the use of engineering approximations and assumptions based on existing technologies allow for an insightful analysis to be made.

Herein, we developed an economic model for a CO₂ electrolyzer system that calculated the material and energy balances for the process, estimated the capital investment and operating costs, and performed a cash flow analysis to determine the end-of-life net present value (NPV). This allowed for the comparison of various CO₂ reduction products, as well as the sensitivity to the potentially changing operating/market conditions. A schematic of the general CO₂ reduction system is shown in Figure 3.

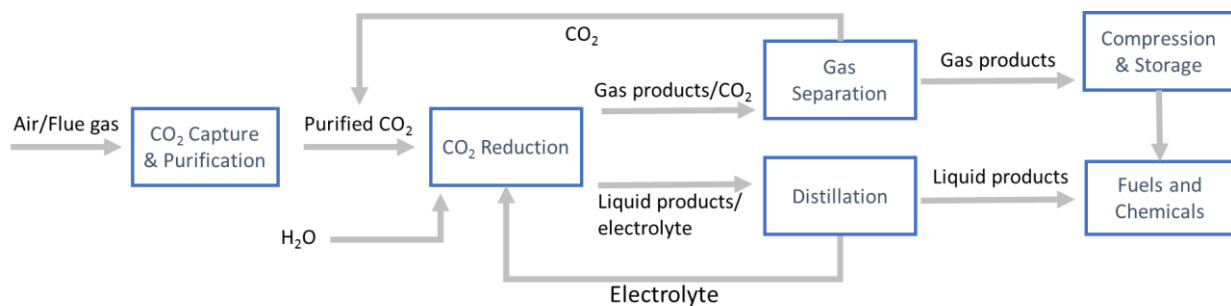


Figure 3: Schematic of a general CO₂ electrolysis process.

In a general eCO₂R process, CO₂ is first captured from either a point source or the air, and purified for use in the CO₂ electrolysis system. The concentrated CO₂ stream is fed along with water to the CO₂ electrolyzer system, where liquid and gas products are formed. The liquid products that are formed in the electrolyte stream are fed to a separation system to extract the liquid products, while the electrolyte is recycled back to the electrolyzer. Since the single pass accumulation for liquid products is typically very small (<0.01%), the electrolyte is recycled until the liquid products accumulate to an appreciable amount before separation. The gas products, along with unconverted CO₂ and byproduct hydrogen, are separated in a gas separation unit, from which the CO₂ is recycled back to the reactor. The gas products are then compressed for storage and transportation, or fed to another downstream chemical process.

5. Modeling of System Components

5.1 CO₂ Capture

To provide an estimate for the capital costs of the CO₂ capture & purification process, various existing technologies were first examined. The CO₂ feedstock for the electrochemical process can be obtained either from a point source such as a power plant or chemical facility, or directly from the atmosphere. The incorporation of CO₂ capture systems to coal and natural gas power plants is currently an area of intense research. The current state-of-the-art involves chemical adsorption using monoethanolamine (MEA) at a cost of \$70 USD per ton of CO₂ captured.⁷⁷ This high cost is the main barrier for the incorporation of CO₂ capture to power plants. Through solvent and process design improvements, the cost of capture could be reduced to as much as \$44 USD per ton CO₂.⁷⁸ Furthermore, the use of CO₂ in an electrochemical conversion to create value added products could also increase the economic viability of capture. One concern of CO₂ capture from point sources is the presence of other combustion products such as SO_x and NO_x compounds. The impact of these compounds on electrolyzer performance is not yet understood, but the CO₂ stream likely needs to be of high purity for stable and efficient conversions.

Alternatively, the capture of CO₂ from air has yet to be commercially developed, although a small demo facility by Climeworks in Switzerland recently opened. The cost estimates for such a system range anywhere between US\$30 – US\$1000 per ton of CO₂.⁷⁹⁻⁸⁰ One advantage of DAC is the portability of the process, which allows for distributed use, which couples well with renewable energy sources. Furthermore, the capture of CO₂ from air represents a net-reduction in CO₂ as opposed to avoided emissions since the CO₂ is being taken from the atmosphere. For the purposes of this analysis, it was assumed that CO₂ was obtained at a base price of US\$100 per ton.

5.2 Electrochemical Cell

Currently, CO₂ electrolyzers exist only at the bench scale. Furthermore, there is no standard design for a CO₂ electrolyzer cell with several configurations reported.^{12-13, 70} To provide an estimate for the capital costs of an electrolyzer system, an alkaline water electrolyzer stack as a representative model was used. In CO₂ electrolysis, non-precious metal catalysts are used, making the alkaline comparison appropriate. Furthermore, the auxiliary systems and balance of plant for a CO₂ electrolyzer are likely to be similar. The main difference would be the electrolyzer design requiring a direct feed of CO₂ to the catalyst surface, which would have a minimal cost difference. The design of the reactor between different products would also be consistent, with the exception being formate requiring protonation to formic acid. This has been demonstrated at the lab scale.¹³

Therefore, the capital and operating costs for the CO₂ electrolyzer were based on the DOE Current Central H2A base case for an alkaline electrolyzer.⁸¹ In this analysis, the uninstalled capital costs were \$327/kW. To make the model sensitive to current density, a cost per surface area was also determined. This cost was calculated based on the typical operating conditions of 175 mA/cm² and 1.75 V for the Norsk Hydro HPE Atmospheric Type No. 5040 alkaline electrolyzer on which the base case was derived from, corresponding to an uninstalled cost of \$1065/m². An installation factor of 1.5 was used for the capital investment. Furthermore, it was assumed that maintenance costs were 2.5% of the capital investment per year. These costs included replenishing the catalysts and electrolytes used in the system. The balance of plant (BoP) costs were assumed to be 20% of the cost of the electrolyzer system, and these values were derived from the H2A model.⁸¹ The only operating cost for the system was electricity, which was calculated based on the Faradaic mass balances across the electrolyzer.

5.3 Product Separation

For gas product separation, pressure swing adsorption is an industrially used process with low operating costs, high efficiency, and limited footprint.⁸² For CO₂ electrolysis, the reactor exit gas consists of unconverted CO₂ and gas products, as well as some hydrogen. A similar separation is the upgrading of biogas, which consists of roughly equal amounts of methane and CO₂. Industrial reports have been developed regarding the costs of biogas upgrading with PSA and allowed for an estimation of the separation costs for CO₂ electrolysis gas product separation based on commercial systems.⁸³⁻⁸⁴ Based on these studies, a reference cost of \$1,990,000 per 1000 m³/hr capacity was used, with a capacity scaling factor of 0.7 and operating costs consisting of only electricity at 0.25 kWh/m³.⁸⁵ After separation, the gas products need to be compressed and stored, unless they are transported to and used immediately in a downstream process. Here, this additional cost was neglected.

Distillation was used as the separation process for the CO₂ reaction liquid products, as alcohols are separated by distillation commercially. Formic acid can also be separated by distillation, although it is highly energy intensive due to the close boiling points of water and formic acid. Furthermore, water was the distillate product leading to a high heat duty needed for the column. Alternatively, BASF utilizes a liquid-liquid extraction process to purify formic acid solutions up to 95% by weight.⁸⁶ However, to allow for consistent comparison, the separation of formic acid was also modeled through distillation. The separation processes were modeled using the RadFrac block in Aspen Plus, and capital and utility costs were estimated using the Aspen Plus Economic Analyzer. An electrolyte flow rate of 1000 L/min was assumed for the base case, with a concentration of 10% product in water. The separation was modeled as a single column with the product leaving near the azeotropic concentration. In practice, more elaborate methods such as extractive or pressure swing distillation would allow for higher product purity. The capital costs were then scaled with a capacity factor of 0.7, while the utility costs were scaled linearly.

6. Model Assumptions

6.1 Base Model Assumptions

To perform a comparison of the various CO₂ reduction products, several process assumptions were made. We considered two sets of parameters: a base case based on current feedstock prices and electrolyzer performance, and an optimistic case that considered what these values may be in the future. These assumptions are summarized in Table 3.

Table 3: Process assumptions for CO₂ electrolyzer model

Parameter	Base Case	Optimistic Case
Production Rate (ton/day)	100	100
Lifetime (years)	20	20
Operating time (days/year)	350	350
Electricity Price (\$/kWh)	0.05	0.03
Current Density (mA/cm ²)	200	300
Cell Voltage (V)	2.3	2
Product Selectivity (%)	90	90
Conversion (%)	50	50
CO ₂ Price (\$/ton)	100	50
Interest Rate (%)	10	7.5
Electrolyzer Cost (\$/m ²)	2830	1415

For both cases, a product production rate of 100 tons/day was chosen to allow for large scale chemical production, for which the capital costs were more favorable and differences between products were more discernable, while keeping the electrolyzer system power requirements within the range of the largest commercial systems (~100 MW). It was assumed that the system would require 2 weeks of downtime each year for maintenance over a 20-year lifetime. The base case electricity price of 0.05 \$/kWh was consistent with the cheapest industrial electricity rates currently available. As renewable energy sources such as solar and wind continue to become cheaper, the price of electricity could be as low as 0.02 \$/kWh.⁸⁷ An optimistic case value of 0.03 \$/kWh was chosen. The electrolyzer total current density of 200 mA/cm² has been demonstrated in numerous laboratory reactors at roughly 2.3 V.⁷⁰ For the optimistic case, a current density of 300 mA/cm² was assumed at cell voltage of 2 V, which fell within the range of commercial water electrolyzers. As shown in Figure 2, Faradaic efficiencies of 90% have been demonstrated for numerous CO₂ reduction products such as CO, formic acid, and methanol, and were assumed for these cases. A baseline reactor conversion of 50% was chosen for the analysis. It must be noted that CO₂ conversion is not often reported in the literature because most of studies are performed in either a batch cell or single-pass flow cell with conversions less than 10%. A better electrolyzer design could potentially boost the CO₂ conversion to 50%. A low conversion results in a more challenging product separation due to the unreacted CO₂ in the reactor effluent that needs to be recycled.

6.2 Financial Model Assumptions

To estimate the return on capital investment for the development of a CO₂ electrolysis facility, a cash flow spreadsheet was developed to estimate the yearly revenue and present value of the plant over the project lifetime. It was assumed that construction of the facility was completed in the first year, with product production beginning in the second year. The working capital was

assumed to be 5% of the capital investment. A MACRS 10-year depreciation schedule was used with a 20% salvage value at the end of plant life. A base case nominal interest rate of 10%, compounded annually, and a total effective income tax rate of 40% were assumed. These financial assumptions were consistent with those in the DOE's H2A analysis for water electrolysis.⁸¹ The yearly profit was calculated as the income from selling product minus the yearly operating costs of the plant. The cost of sales, cost of labor, and inflation were not accounted for in the financial model. From this model, the net present value of the facility at the end of life was calculated.

7. Economic Cost Analysis

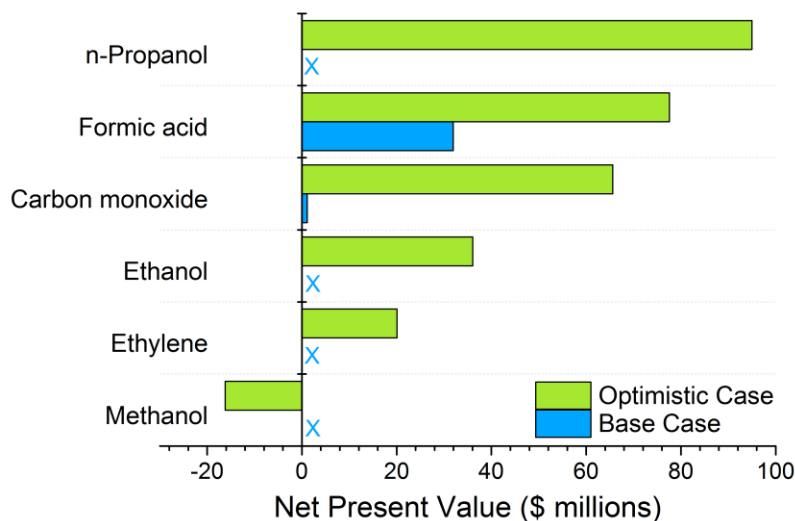


Figure 4: End-of-life NPV values for the production of various chemicals.

The net present value for the main products using the base case and optimistic case assumptions are shown in Figure 4. Methane is not shown because its current market value was lower than the price of CO₂, making profitability impossible regardless of process performance. The X's indicate that the production was not profitable on a yearly basis, so the NPV could not be calculated.

At the base case conditions, CO and formic acid were the only profitable products for the CO₂ electrolysis system, whereas the other products were not even profitable on a yearly basis. This is because CO and formic acid have the highest product value per electron (Table 2). Even at a modest electricity cost of \$0.05/kWh, the amount of electricity needed to produce hydrocarbons and alcohols outweighed the values of the chemical products. However, these products became much more favorable under the optimistic case assumptions. The production of n-propanol was the most favorable product, with methanol being the only product with a negative NPV. Based on CO₂ reduction studies in the literature, selectively obtaining n-propanol as the sole product is likely to be a major challenge, as the selectivity towards n-propanol is still quite low. However, a mixture of these liquid C₂-C₃ alcohols would still be economically valuable since ethanol was also favorable under the optimistic case.

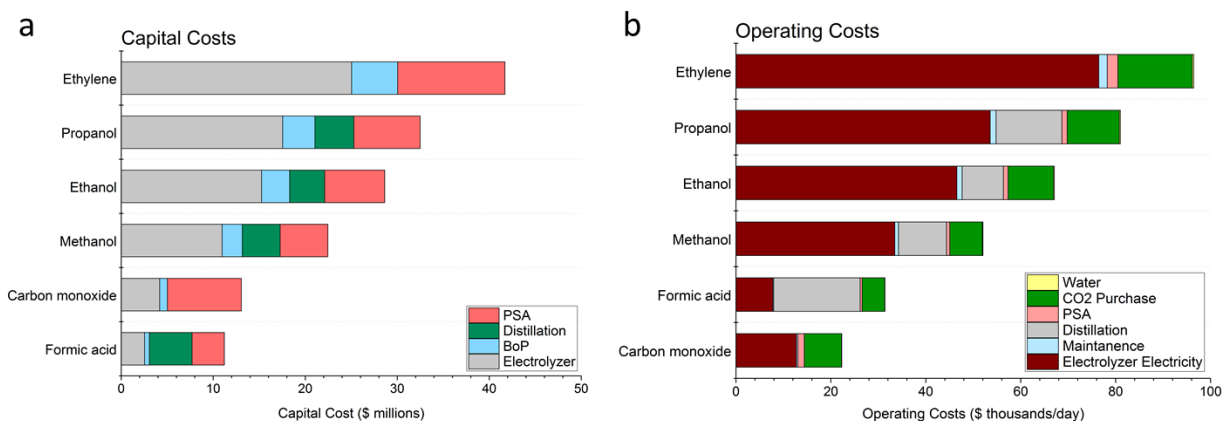


Figure 5: a) Capital and b) operating costs for various products under optimistic case assumptions.

To give a relative sense of the various costs of the process, the breakdown of capital and operating costs for each product under optimistic case assumptions are shown in Figure 5. Of all products, ethylene had the highest capital and operating costs due to the large amount of current (electricity) needed per kg of product. These high costs, along with a large CO₂ feedstock requirement, contributed to the low profitability of ethylene relative to other products. In contrast, formic acid and CO benefited from a small power requirement, which reduced the cost of electricity and electrolyzer size. For formic acid, much of the cost was associated with the challenging distillation process. As stated earlier, there are industrial processes that may be more cost effective than distillation, which could further improve the profitability of formic acid. For example, a 50% reduction in the operating and capital costs for formic acid separation gave an NPV of \$97.1 million. It must be noted, that while the distillation and PSA systems had similar capital investment requirements, the PSA systems had a much lower operating cost. Although this cheaper separation was an advantage for gaseous products, they will likely require additional compression for transportation/storage, which could increase costs significantly.

To understand the sensitivity of the process profitability to different parameters, a sensitivity analysis was performed. The range of values considered for each parameter is listed in Table 4, with the results shown in Figure 6.

Table 4: Range of values for sensitivity analysis

Sensitivity Parameters	Better	Base	Worse
Electric Price (\$/kWh)	0.02	0.03	0.04
Selling Price (\$/kg)	+15%	Base	-15%
Selectivity (%)	80	90	100
Voltage (V)	1.7	2	2.3
Electrolyzer Cost (\$/m ²)	707.5	1415	2830
CO ₂ Cost (\$/ton)	0	50	100
Current Density (mA/cm ²)	500	300	100
Conversion (%)	70	50	30

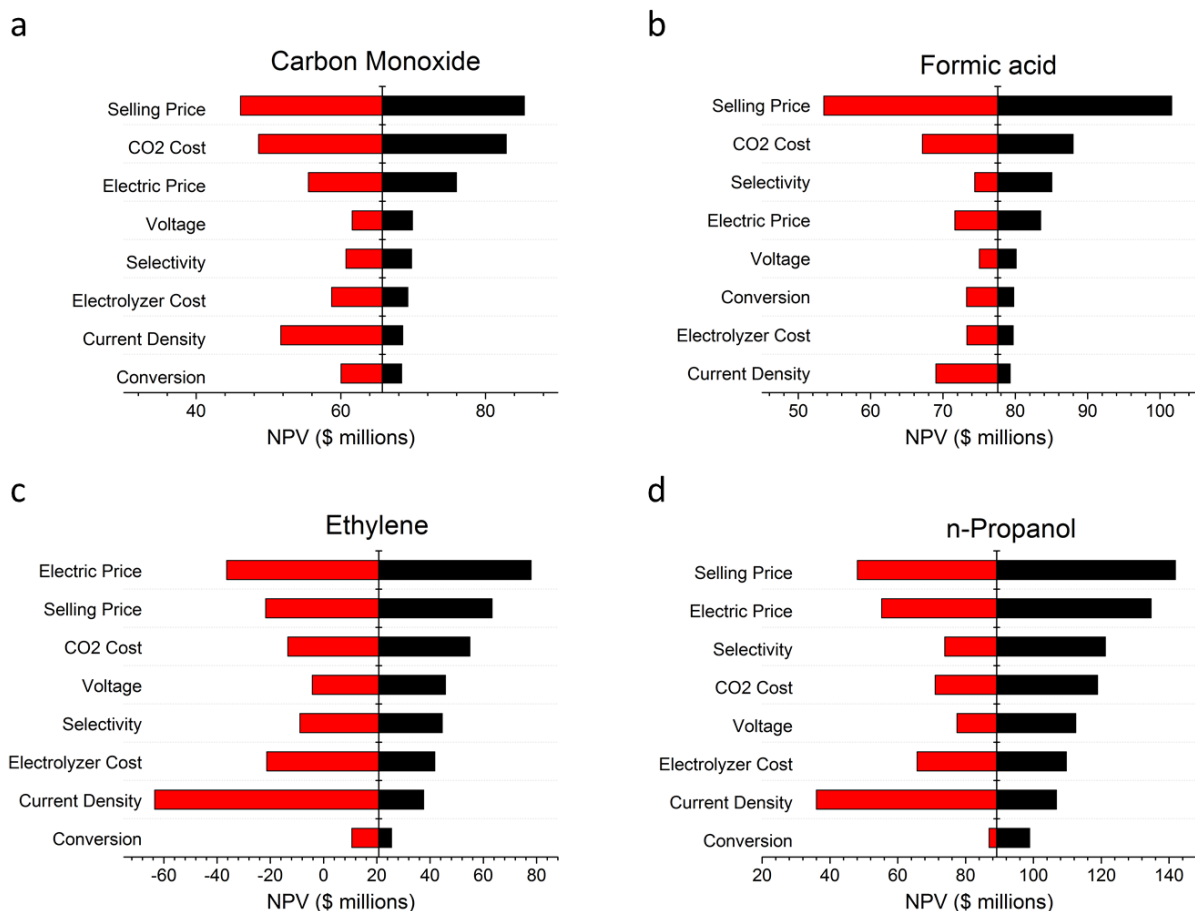


Figure 6: Sensitivity analysis of CO₂ reduction products: a) carbon monoxide, b) formic acid, c) ethylene, and d) n-propanol.

For all products, a deviation in selling price of 15% had a significant impact on the end-of-life NPV of the process. Over a 20-year period, the product price could fluctuate significantly due to changes in market demand and development of new technologies. Therefore, the production of products such as CO, n-propanol, and formic acid are advantageous since they remained profitable even if the product selling price dropped significantly. For all products other than CO and formic acid, electricity was the major operating cost, resulting in a strong economic dependence on the price of electricity. Even a change of just \$0.01/kWh resulted in a NPV difference of \$40 million for n-propanol production. Therefore, it is critical for the CO₂ electrolyzer to have a steady supply of cheap electricity if hydrocarbons and alcohols are produced, which could be obtained through renewable sources in the near future.⁸⁷

In terms of electrolyzer performance, selectivity and voltage were the most important parameters for higher electron products such as alcohols and ethylene. A higher selectivity reduced the total current needed because less electricity was wasted on hydrogen generation. This led to a lower power requirement and subsequently a lower electricity operating cost. Less hydrogen also reduced the separation requirement for recycling the CO₂, which was a significant cost even for liquid products. Also, a decrease in total current reduced the total electrolyzer area, resulting in a lower electrolyzer capital cost. Reducing the cell voltage (overpotentials) lowered the overall

power requirement, which significantly impacted products with high electricity operating cost fraction. Furthermore, the reactor conversion also impacted the economics. A lower reactor conversion resulted in a higher separation cost due to an increased amount of unconverted CO₂ in the separation/recycle loop, and this consequentially increased the size/capital cost of the PSA system. However, in the case of low conversion and high selectivity towards liquid products, the gas stream exiting the reactor consisted almost entirely of CO₂ with some residual hydrogen. Thus, multiple passes were made before separation, as a small dilution of the CO₂ feedstock did not significantly influence reactor performance.

Interestingly, the current density was the least important parameter of electrolyzer performance once above a certain threshold. This was due to the inverse square relationship between the electrolyzer capital cost and current density. Thus, for products that required large amounts of electricity, increasing the current density to at least 250-300 mA/cm² was critical. In the case of ethanol, a decrease in current density to 100 mA/cm² resulted in a NPV decrease of \$51 million, while an increase to 500 mA/cm² only gave an extra \$10 million (Supplementary Figure S1). After a certain threshold, the capital costs of the electrolyzer, which were directly influenced by current density, became insignificant to the other costs. Stemming from these calculations, since the cell voltage was a significant cost due to the extra power requirement, the CO₂ electrolyzer should operate at as low of a voltage possible while still maintaining an appreciable current density.

8. Catalyst Activity Targets

The CO₂ electrolyzer model was used to define activity targets for electrolyzer performance needed to be profitable for a given CO₂ reduction product. As shown in the sensitivity analysis, cell potential and selectivity were the major parameters. Since the anode of the CO₂ electrolyzer is typically water oxidation, and anion exchange membrane development is vastly improving, the cell potential was simplified to the overpotential associated with the electrochemical reduction of CO₂. We assumed the optimistic base case conditions with a current density of 300 mA/cm². The anodic overpotential was estimated as 0.3 V with a cell resistance overpotential of 0.1 V. Figure 7 shows the overpotential/selectivity performance curves for various products needed to obtain an end-of-life NPV of \$0 (IRR of 7.5%). For the process to be profitable, the electrolyzer performance must lie to the right of the curve. It can be seen that the production of CO and formic acid can be done profitably under the optimistic base conditions with relatively poor electrolyzer performance, requiring Faradaic efficiencies much lower than currently obtained. However, n-propanol requires a modest selectivity, while ethanol and ethylene require relatively high Faradaic efficiencies. Altogether, it is promising that the activity targets for the profitable production of these hydrocarbon and alcohol products are feasible, as they have a much larger market potential compared to CO and formic acid.

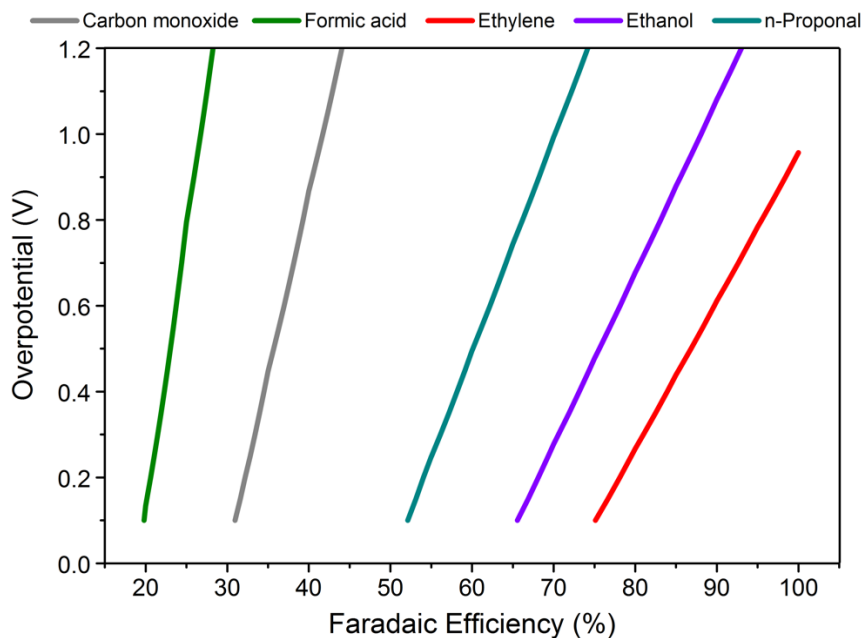


Figure 7: Electrolyzer performance curves for an IRR of 7.5%.

9. CO₂ Emissions Reduction

Although eCO₂R has the potential to profitably produce valuable chemical feedstocks, it is unlikely that the technology alone can significantly reduce the atmospheric CO₂ concentration for a couple of reasons. Firstly, as discussed early, the direct air capture of CO₂ is still expensive. Secondly, the total amount of CO₂ emission is too large to be handled by electrochemical processes alone. Per the EIA, the US emitted roughly 5.2 MMmt of CO₂ from the energy-sector alone in 2015. Reducing this CO₂ to a two-electron product like formic acid would require ~1.5 TW, which is equivalent to roughly 8% of the world's energy output.

However, if low-carbon electricity sources such as wind and solar are used, additional CO₂ emissions can be mitigated if the CO₂ is sourced from industrial sources such as fossil fuel power plants and chemical facilities, since converting this CO₂ through eCO₂R would then be a reduction of emissions as opposed to the commonly used case where the CO₂ is simply emitted. This is true even if the CO₂ reduction product is a fuel that is later burned, provided it replaces those derived from fossil fuels. For example, consider the electrochemical reduction of CO₂ to ethanol for use as a fuel additive. We estimated the greenhouse gas emissions (reported as grams of CO₂ equivalent) for the process associated with the electricity used, as this is the major operating cost. Additional emissions would result from construction of the facility materials and other process costs (steam, heating, etc.), which were not considered as they are assumed to be small, compared to the electrical system. Despite being “renewable” sources, wind and solar have some associated emissions due to construction and maintenance.⁸⁸ As illustrated in Figure 8, the associated emissions with the electrochemical production of ethanol from CO₂ are much less than those of gasoline, and comparable to ethanol derived from corn feedstocks, which is the current dominant production method.⁸⁹ This shows that CO₂-derived chemicals and fuels can indirectly lead to a reduction of CO₂ emissions.

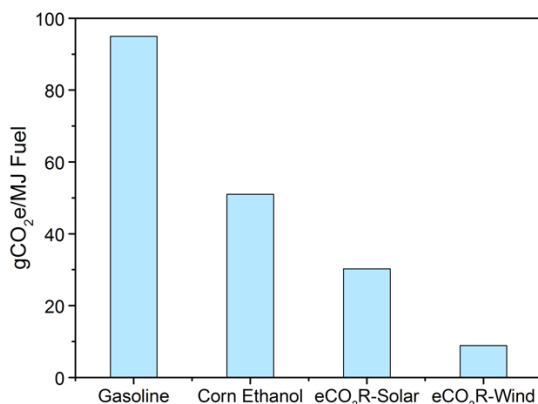


Figure 8: Greenhouse gas emissions for the production of gasoline and corn ethanol (ref. 89) compared to electrochemical CO₂ reduction

10. Conclusions

The generalized techno-economic model for eCO₂R presented in this work provides insight into the feasibility of various common CO₂ reduction products for large-scale chemical production. We found that current density is the least important electrolyzer parameter after a certain threshold (200-400 mA) is reached, while selectivity and overpotential are critical, especially for high-electron products. Simple products such as CO and formic acid were more profitable under current economic conditions and performance based on the current state-of-the-art electrocatalysts, although only lab-scale electrolyzer systems have been demonstrated. However, the small market potential for formic acid and the difficulty associated with storing/transporting gaseous products motivates the production of liquids such as ethanol and n-propanol, which could be profitable under more favorable economic conditions in the future and may have a much higher market potential. For higher-order alcohols to become profitable, cheaper electricity costs and improved catalytic performance are needed. However, with continual efforts, the electrocatalytic performance benchmarks for these alcohols can be achievable, and the use of C₂-C₃ alcohols produced from eCO₂R would allow for renewable energy sources to penetrate into the transportation and chemical sectors while potentially reducing GHG emissions. Overall, the electrochemical reduction of CO₂ is a promising technology that could play a significant role in the future renewable energy infrastructure if further strides are made.

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